

## Can Chlorine Anion Catalyze the Reaction of HOCl with HCl?

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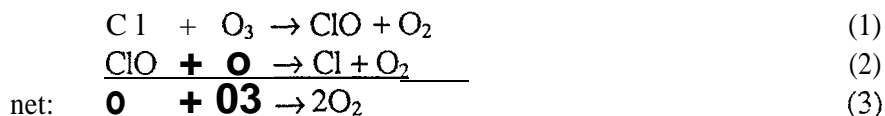
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### Abstract

The reaction of  $\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$  in the presence of Cl has been studied using *ab initio* methods. This reaction has been shown to have a high activation barrier of  $46.5 \text{ kcal mol}^{-1}$ . The chlorine anion, Cl<sup>-</sup> is found to catalyze the reaction, viz. two mechanisms. The first involves Cl<sup>-</sup> interacting through the concerted four-center transition state of the neutral reaction. The other mechanism involves the formation of a  $\text{HCl} \cdot \text{HOCl} \cdot \text{Cl}^-$  intermediate which dissociates into  $\text{Cl}_2 + \text{Cl}^- + \text{H}_2\text{O}$ . The steps are found to have no barriers. The overall exothermicity is  $15.5 \text{ kcal mol}^{-1}$ .

Understanding the underlying chemistry behind stratospheric ozone depletion is central to finding ways of curtailing further loss of ozone in the Antarctic Ozone Hole. One of the major reaction processes implicated in the catalytic removal of ozone is the heterogeneous reaction of HCl with  $\text{ClONO}_2$  to give  $\text{HNO}_3$  and  $\text{Cl}_2$ .<sup>1,2,3</sup> The  $\text{Cl}_2$  can subsequently photolyze to produce Cl atoms which can then participate in homogeneous catalytic cycles for ozone destruction through

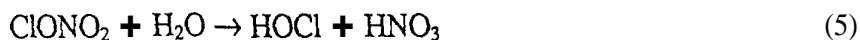


Recent field measurements of HCl and ClO concentrations in the stratosphere show that the reaction of HCl with  $\text{ClONO}_2$  is critical in determining the winter and spring chlorine budget

within the polar vortex.<sup>4,5</sup> However, extensive experimental studies suggest that the heterogeneous reaction of HCl with ClONO<sub>2</sub>,



may not occur in one step but two viz.<sup>6,7,8</sup>



The net reaction of steps 5 and 6 is reaction 3.

A key step is the reaction involving HOCl with HCl (reaction 6). Experimentally,<sup>9</sup> this reaction is known to be slow in the gas-phase; but little is known about the details of the energetic that could explain the slow rate. Abbatt et al.<sup>6,7</sup> have asserted that reaction 6 can occur on polar stratospheric cloud (PSC) particles. However, the existence of solvated chlorine in the form of Cl<sup>-</sup> on PSC particles has been suggested.<sup>5,6,7</sup> This has raised the question of whether Cl<sup>-</sup> can catalyze the reaction of HOCl with HCl (reaction 6). In this paper we use *ab initio* calculations to ascertain if Cl<sup>-</sup> can lower the activation barrier for the HOCl + HCl reaction.

The geometries of reactants, products and transition states have been optimized using the *ab initio* MP2 method.<sup>10</sup> Two basis sets have been used for optimization: 6-31G(d) and 6-311++G(2d,2p) which includes diffuse- and p-functions and an extra set of d-functions on all heavy atoms. The diffuse functions are added because we believe these to be essential for accurate description of geometries and energetic for anions. Single point energies have been calculated using the CCSD(T) method with the extend 6-311++G(3df,3pd) basis set.

Geometries of the transition state for the reaction of HOCl + HCl → Cl<sub>2</sub> + H<sub>2</sub>O is shown in Figure 1a. The number without the asterisk are geometric parameters that have been calculated at the MP2/6-31G(d) level, and the numbers with the asterisk are at the MP2/6-311++G(2d,2p). The transition state is a four-center reaction. The HCl approaches HOCl orienting the hydrogen

of the HCl toward the oxygen of HOCl. The HCl bond length increases from the length of the HCl bond in isolated hydrogen chloride. The ClO bond length also increases from that in HOCl. The transition state is a non-planar structure. The four atoms involved in the four-center ring is out-of-plane by  $5.9^\circ$ . Moreover, the hydrogen on HOCl is out of the plane of the ClOH' group by  $98^\circ$ . The transition state is a true first-order saddle point, with one negative frequency.<sup>11</sup> The relative energetic are given in Table 1. The experimental heat of reaction<sup>12</sup> at OK for the HOCl + HCl reaction is  $-18.0 \text{ kcal mol}^{-1}$ . At the CCSD(T)/6-311++G(3df,3pd) level we predict a value of  $-15.4 \text{ kcal mol}^{-1}$ , which is in reasonable agreement with the experimental results. The calculated barrier of the same level of theory is  $46.5 \text{ kcal mol}^{-1}$ . Such a high barrier suggest that the homogeneous reaction will be very slow which is consistent with the experimental observations.

In the presence of Cl<sup>-</sup>, the anion prefers completing through the hydrogen not involved in the four-center ring. The anion has a dramatic effect on the transition state. The transition state along with structural parameters are given in Figure 1b. The transition state is also a first-order saddle point with one imaginary frequency.<sup>13</sup> Comparing the HCl bond, this bond is longer in the transition state involving the anion than without the anion present. The ClO bond in the transition is significantly elongated as a result of the Cl<sup>-</sup>. It is also interesting to note that the atoms in the four center ring is more out-of-plane than in the neutral reaction;  $24.0^\circ$  versus  $5.9^\circ$ , respectively. These changes in the transition state for HOCl + HCl involving Cl<sup>-</sup> compared to without the Cl<sup>-</sup> indicate that the transition state occurs earlier in the entrance channel. The structural changes in the transition state also suggest that breaking the ClO bond in HOCl and the HCl bond in HCl in the transition state is easier by the presence of the Cl<sup>-</sup>. The activation barrier for HOCl + HCl + Cl<sup>-</sup> formation is  $8.3 \text{ kcal mol}^{-1}$  at the CCSD(T)/6-311++G(3df,3pd) level. The activation barrier for the neutral reaction (3) is found to be very high and the reaction is slow. However,

involvement of Cl<sup>-</sup> anion dramatically changes the potential energy surface. These calculations shows that the involvement of the anion lowers the neutral barrier by 38.2 kcal mol<sup>-1</sup>. Moreover, these calculations suggest that the anion could play a significant role in reducing the energetic of the HOCl + HCl reaction.

While exploring the potential energy surface of the HOCl + HCl reaction in the presence of Cl<sup>-</sup>, we found an alternate mechanism for the formation of the Cl<sub>2</sub> + H<sub>2</sub>O products. A stepwise mechanism involving the formation of anion complexes such as Cl<sup>-</sup>·HOCl and Cl<sup>-</sup>·H<sub>2</sub>O was found. The Cl<sup>-</sup>·HOCl anionic complex reacts with HCl in a barrier-less process to form a HCl · HOCl · Cl<sup>-</sup> intermediate. This intermediate is shown in Figure 2. At the MP2/6-31G(d) level, the ClO bond in the HCl · HOCl · Cl<sup>-</sup> intermediate is elongated nearly 0.6 Å from the ClO bond in HOCl, and the H'Cl bond is elongated by 0.7 Å from the uncomplexed HCl. We have performed a vibrational frequency analysis to determine if the intermediate is a saddle or minimum energy point on the potential energy surface.<sup>14</sup> The vibrational energy calculations reveal that the structure has all real and positive frequencies. The energy of the intermediate formation from the reaction of HCl + HOCl and Cl<sup>-</sup> is calculated to be -37.3 kcal mol<sup>-1</sup> at the MP2/6-31G(d) levels, and reduces to -38.0 kcal mol<sup>-1</sup> at the CCSD(T)/6-311++G(3df,3pd) level. The formation of Cl<sub>2</sub> + H<sub>2</sub>O + Cl<sup>-</sup> requires 22.5 kcal mol<sup>-1</sup> at the CCSD(T) level. As a result, one can view an alternate mechanism for HCl + HOCl catalysis by Cl<sup>-</sup> as involving a step-wise mechanism first involving the formation of a Cl<sup>-</sup> · HOCl complex which then attaches to HCl forming an HCl · HOCl · Cl<sup>-</sup> intermediate. The next step involves the detachment of Cl<sub>2</sub> and Cl<sup>-</sup> · H<sub>2</sub>O complex. At low temperatures this mechanism involving the HCl · HOCl · Cl<sup>-</sup> intermediate may be preferable. We should point-out that such an attachment/detachment mechanisms has been suggested for the reaction of HCl with ClONO<sub>2</sub> catalyzed by NO<sub>3</sub><sup>-</sup>.

More importantly, the present calculations suggest that anions, such as  $\text{Cl}^-$ , can play a major role in promoting the reaction of  $\text{HOCl}$  with  $\text{HCl}$ . The energetic effects on the  $\text{HOCl} + \text{HCl}$  reaction are considerable. Moreover, anions such as nitrate and/or sulfate which are important ions in atmospheric aerosols may play similar roles in the energetic of the  $\text{HOCl}$  with  $\text{HCl}$  reaction.

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- <sup>11</sup> Vibrational frequencies at the MP2/6-31G(d) level of theory for the neutral  $\text{HCl} + \text{HOCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$  reaction are: 3604,2041, 1598,948, 811,365,318,222, 1288 *i* cm<sup>-1</sup>.
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- <sup>13</sup> Vibrational frequencies at the MP2/6-31G(d) level of theory for the  $[\text{HCl} + \text{HOCl} + \text{Cl}]^\ddagger$  transition state are: 3273, 1751, 1544, 1046, 891, 552, 352, 271, 232, 67, 49, 643 *i* cm<sup>-1</sup>.
- <sup>14</sup> Vibrational frequencies at the MP2/6-31G(d) level of theory for the  $\text{HCl} \cdot \text{HOCl} \cdot \text{Cl}^-$  intermediate are: 3793, 2999, 1746, 959, 606, 384, 370, 321, 201, 162, 136, 39 cm<sup>-1</sup>.
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Table 1 Relative Energetics (in kcal mol<sup>-1</sup>) with Respect to HOCl + HCl Catalyzed by Cl<sup>-</sup>

Level of Theory	$\text{HOCl} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$		$[\text{HOCl} + \text{HCl} + \text{Cl}]^\ddagger$	$\text{Cl}^- + \text{HOCl} + \text{HCl} \rightarrow$ $\text{HOCl} \cdot \text{HOCl} \cdot \text{Cl}^-$		$\text{HCl} \cdot \text{HOCl} \cdot \text{Cl} \rightarrow$ $\text{Cl}_2 + \text{H}_2\text{O} + \text{Cl}^-$
	$\Delta H_{\text{r},\text{o}}$	$H^\ddagger$	$H^\ddagger$	$\Delta H_{\text{r},\text{o}}^0$		$\Delta H_{\text{r},\text{o}}^0$
MP2/6-31G(d)	-10.1	52.3	8.1	-37.3		27.2
MP2/6-311++G(2d,2p)	-16.8	49.7	10.3	-41.4		24.6
CCSD(T)/6-311++G(3df,3pd) <sup>a</sup>	-15.5	46.5	8.3	-38.0		22.5
Experiment	- 8 °					

<sup>a</sup> Geometries from the MP2/6-311++G(2d,2p) level are used.

## Figure Captions

Figure 1. (a) Transition state for  $\text{HCl} + \text{HOCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O}$  for the neutral reaction. Numbers without asterisk are calculated at the MP2/6-31G(d) level, numbers with the asterisk are at the MP2/6-311++G(2d,2p) level of theory.

(b) Transition state for  $\text{HCl} + \text{HOCl} + \text{Cl}^- + \text{Cl}_2 + \text{H}_2\text{O} + \text{Cl}^-$  with  $\text{Cl}^-$  interacting through the four-center  $\text{HCl} + \text{HOCl}$  transition state. Numbers without asterisk are calculated at the MP2/6-31G(d) level, numbers with the asterisk are at the MP2/6-311++G(2d,2p) level of theory.

Figure 2.  $\text{HCl} \cdot \text{HOCl} \cdot \text{Cl}^-$  intermediate. Numbers without asterisk are calculated at the MP2/6-31G(d) level, numbers with the asterisk are at the MP2/6-311++G(2d,2p) level of theory.



